

TITLE OF THE INVENTION

RADIATION-SENSITIVE RESIN COMPOSITION

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a radiation-sensitive resin composition and, more particularly, to a radiation-sensitive resin composition suitable as a chemically-amplified resist useful for microfabrication utilizing various types of radiation, for example, deep ultraviolet rays such as a KrF excimer laser or ArF excimer laser, X-rays such as synchrotron radiation, or charged particle rays such as electron beams.

Description of the Background Art

15 In the field of microfabrication represented by fabrication of integrated circuit devices, lithographic technology enabling microfabrication with a line width of 0.20  $\mu\text{m}$  or less has been demanded in order to achieve a higher degree of integration.

20 A conventional lithographic process utilizes near ultraviolet rays such as an i-line radiation. It is known in the art that microfabrication with a line width of sub-quarter micron using near ultraviolet rays is very difficult.

25 Therefore, use of radiation with a shorter wavelength has been studied for enabling microfabrication with a line width of 0.20  $\mu\text{m}$  or less. Deep ultraviolet rays represented by a line spectrum of a mercury lamp and an excimer laser, X-rays,

electron beams, and the like can be given as radiation with a shorter wavelength. Of these, a KrF excimer laser (wavelength: 248 nm) and an ArF excimer laser (wavelength: 193 nm) have attracted attention.

As a resist applicable to the excimer laser radiation, a number of resists utilizing a chemical amplification effect between a component having an acid-dissociable functional group and a component generating an acid (hereinafter referred to as "photoacid generator") which generates an acid upon irradiation (hereinafter referred to as "exposure") has been proposed. Such a resist is hereinafter called a chemically-amplified resist.

As such a chemically-amplified resist, Japanese Patent Publication No. 27660/1990 discloses a resist comprising a polymer containing a t-butyl ester group of carboxylic acid or a t-butylcarbonate group of phenol and a photoacid generator. The t-butyl ester group or t-butyl carbonate group in the polymer dissociates by the action of an acid generated upon exposure, whereby the polymer has an acidic group such as a carboxylic group or a phenolic hydroxyl group. As a result, exposed areas of the resist film become readily soluble in an alkaline developer.

Most of conventional chemically-amplified resists use a phenol resin as a base resin. Deep ultraviolet rays used as radiation for exposure are absorbed due to an aromatic ring in the resin and cannot sufficiently reach the lower layers of the resist film. Because of this, the dose of the radiation is

greater in the upper layers and is smaller in the lower layers of the resist film. This causes a resist pattern to be slimmer in the upper portion but broader toward the lower portion, thereby forming a trapezoid shape after development. No sufficient resolution can be obtained from such a resist film. Such a trapezoid resist pattern formed after development cannot give a desirable dimensional accuracy in the succeeding steps such as an etching step and an ion implantation step. In addition, if the configuration of the upper resist pattern is not rectangular, the resist disappears faster during dry etching, making it difficult to control etching conditions.

The shape of the resist pattern can be improved by increasing the radiation transmittance through the resist film. For example, (meth)acrylate resins represented by polymethylmethacrylate are desirable from the viewpoint of radiation transmittance due to superior transparency to deep ultraviolet rays. Japanese Patent Application Laid-open No. 226461/1992 proposes a chemically-amplified resist using a methacrylate resin, for example. However, in spite of the excellent micro-processing performance, this composition exhibits only poor dry etching resistance due to the absence of an aromatic ring, giving rise to difficulty in performing etching with high accuracy. This composition thus does not have both radiation transmittance and dry etching resistance at the same time.

As a means to improve dry etching resistance of the chemically-amplified resist without impairing the radiation

transmittance, a method for introducing aliphatic rings into the resin component of the resist instead of aromatic rings has been known. For example, Japanese Patent Application Laid-open No. 234511/1995 discloses a chemically-amplified resist using a (meth)acrylate resin having aliphatic rings.

This resist includes groups which comparatively easily dissociate by conventional acids (acetal functional groups such as tetrahydropyranyl group, for example) and groups which are comparatively difficult to dissociate by acids (t-butyl functional groups such as t-butyl ester group or t-butylcarbonate group, for example) as acid-dissociable functional groups in the resin component. The resin component having the former acid-dissociable functional groups exhibits excellent basic characteristics as a resist, in particular, superior sensitivity and excellent pattern shape, but has poor storage stability as the composition. The resin component having the latter acid-dissociable functional groups has excellent storage stability, but exhibits impaired resist characteristics such as sensitivity and pattern shape.

Moreover, inclusion of aliphatic rings in the resin component of this resist results in poor adhesion to substrates due to the extreme increase in hydrophobicity of the resin.

When forming a resist pattern using a chemically amplified resist, the resist is usually heated after exposure to accelerate dissociation of the acid-dissociable group. In this instance, if the heating temperature fluctuates, the resist pattern line width also fluctuates inevitably to a

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certain extent. However, to satisfy the requirement for  
microfabrication of integrated circuit elements in recent years,  
development of a resist exhibiting a small line width  
fluctuation according the heating temperature after exposure,  
i.e. exhibiting small temperature dependency, has been desired.

In addition, the photoacid generator is known to greatly  
affect the functions of a chemically-amplified resist.  
Presently, onium salt compounds which generate an acid upon  
exposure at a high quantum yield and exhibit high sensitivity  
are widely used as a photoacid generator for  
chemically-amplified resists.

As such onium salt compounds, triphenylsulfonium  
trifluoromethane sulfonate, triphenylsulfonium  
hexafluoroantimonite, triphenylsulfonium  
naphthalenesulfonate,  
cyclohexylmethyl(2-oxocyclohexyl)sulfonium  
trifluoromethanesulfonate, and the like are used. Most of  
these conventional onium salt compounds, however, do not  
exhibit satisfactory sensitivity. Although some compounds may  
exhibit comparatively high sensitivity, they are not  
necessarily satisfactory in overall resist performance such as  
resolution, pattern configuration, and the like.

In view of development of technology capable of dealing  
with recent progress in microfabrication of integrated circuit  
devices, a chemically-amplified resist which is applicable to  
short wavelength radiation represented by deep ultraviolet rays,  
exhibits high radiation transmittance, and excels in basic

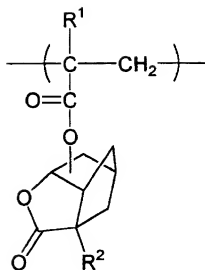
characteristics as a resist such as sensitivity, resolution, dry etching resistance, and pattern shape has been strongly demanded.

An object of the present invention is to provide a  
5 radiation-sensitive resin composition useful as a chemically amplified resist having high transmittance of radiation and exhibiting superior basic properties as a resist such as high sensitivity, resolution, dry etching tolerance, and pattern shape.

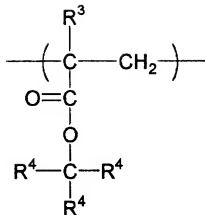
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SUMMARY OF THE INVENTION

The above object can be achieved in the present invention by a radiation-sensitive resin composition comprising:

(A) an acid-dissociable group-containing resin which is  
15 insoluble or scarcely soluble in alkali and becomes alkali soluble when the acid-dissociable group dissociates, the resin comprising the recurring unit of the following formula (1) and the recurring unit of the following formula (2),



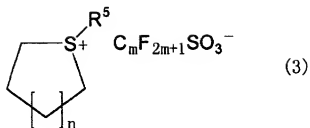
(1)



(2)

wherein R<sup>1</sup> and R<sup>2</sup> individually represent a hydrogen atom or methyl group, R<sup>3</sup> represents a hydrogen atom or methyl group, and R<sup>4</sup> individually represents a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, or any two of R<sup>4</sup> groups form in combination a divalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, with the remaining R<sup>4</sup> group being a linear or branched alkyl group having 1-4 carbon atoms or a monovalent alicyclic hydrocarbon group having 4-20 carbon atoms or a derivative thereof, and

(B) a photoacid generator of the following formula (3),



wherein  $\text{R}^5$  represents a monovalent aromatic hydrocarbon group having 6-20 carbon atoms or a derivative thereof,  $m$  is an integer of 1-8, and  $n$  is an integer of 0-5.

Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

## DETAILED DESCRIPTION OF THE INVENTION

### AND PREFERRED EMBODIMENTS

The present invention will be described in detail below.

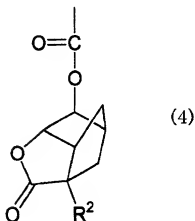
#### (A) Resin

The component (A) of the present invention is an acid-dissociable group-containing resin having a recurring unit of the above formula (1) (hereinafter referred to as "recurring unit (1)") and a recurring unit of the above formula (2) (hereinafter referred to as "recurring unit (2)"). The resin is insoluble or scarcely soluble in alkali, but becomes alkali soluble when the acid-dissociable group dissociates (this resin is hereinafter referred to as "resin (A)").



If 50% or more of the initial film thickness of a resist film remains after development when a resist film made only from the resin (A) is developed under the same alkaline development conditions employed for forming a resist pattern using a resist film formed from a radiation-sensitive resin composition comprising the resin (A), such a characteristic of the resin (A) is referred to as "insoluble or scarcely soluble in alkali" in the present invention.

The carbonyloxy group combined with the main chain of the recurring unit (1) may bond with a carbon atom at any optional position other than the carbon atoms forming a lactone group in the ring or the carbon atom with which the group  $R^2$  bonds, with the position shown in the following formula (4) being preferable.



Preferable examples of the recurring unit (1) include: an acrylic recurring unit having a hydrogen atom for  $R^2$ , a

carbonyloxy group combined with the main chain at the position shown in the above formula (4), and a hydrogen atom for R<sup>1</sup>; a methacrylic recurring unit having a hydrogen atom for R<sup>2</sup>, a carbonyloxy group combined with the main chain at the position shown in the above formula (4), and a methyl group for R<sup>1</sup>; an acrylic recurring unit having a methyl group for R<sup>2</sup>, a carbonyloxy group combined with the main chain at the position shown in the above formula (4), and a hydrogen atom for R<sup>1</sup>; and a methacrylic recurring unit having a methyl group for R<sup>2</sup>, a carbonyloxy group combined with the main chain at the position shown in the above formula (4), and a methyl group for R<sup>1</sup>.

The recurring unit (1) may be used in the resin (A) either individually or in combination of two or more.

The recurring unit (1) is a unit derived from a corresponding (meth)acrylic acid ester.

As examples of the linear or branched alkyl group having 1-4 carbon atoms for R<sup>4</sup> in the recurring unit (2), a methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, 2-methylpropyl group, 1-methylpropyl group, and t-butyl group can be given.

Of these alkyl groups, a methyl group and ethyl group are particularly preferable.

As examples of the monovalent alicyclic hydrocarbon group having 4-20 carbon atoms and the divalent alicyclic hydrocarbon group having 4-20 carbon atoms formed by two R<sup>4</sup> groups, alicyclic groups derived from a cycloalkane such as a norbornane, tricyclodecane, tetracyclododecane, adamantane,

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cyclobutane, cyclopentane, cyclohexane, cycloheptane, or cyclooctane, and groups obtained by replacing hydrogen atoms on these alicyclic groups with one or more linear, branched, or cyclic alkyl groups having 1-4 carbon atoms, such as methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, 2-methylpropyl group, 1-methylpropyl group, or t-butyl group, can be given.

Of these monovalent and divalent alicyclic hydrocarbon groups, alicyclic groups derived from norbornane, tricyclodecane, tetracyclododecane, or adamantane, groups in which a hydrogen atom on these aliphatic rings is replaced by the above alkyl group are preferable.

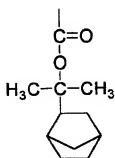
As examples of the derivatives of the above monovalent or divalent alicyclic hydrocarbon groups, groups having one or more substituents such as a hydroxyl group; a carboxyl group; a hydroxyalkyl group having 1-4 carbon atoms such as a hydroxymethyl group, 1-hydroxyethyl group, 2-hydroxyethyl group, 1-hydroxypropyl group, 2-hydroxypropyl group, 3-hydroxypropyl group, 1-hydroxybutyl group, 2-hydroxybutyl group, 3-hydroxybutyl group, and 4-hydroxybutyl group; an alkoxy group having 1-4 carbon atoms such as a methoxy group, ethoxy group, n-propoxy group, i-propoxy group, n-butoxy group, 2-methylpropoxy group, 1-methylpropoxy group, and t-butoxy group; a cyano group; a cyanoalkyl group having 2-5 carbon atoms such as a cyanomethyl group, 2-cyanoethyl group, 3-cyanopropyl group, and 4-cyanobutyl group; and the like can be given.

Of these substituents, a hydroxyl group, carboxyl group,

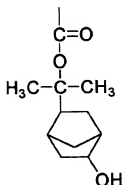
hydroxymethyl group, cyano group, cyanomethyl group, and the like are preferable.

The group  $-\text{COOC}(\text{R}^4)_3$  in the recurring unit (2) is an acid-dissociable group which dissociates in the presence of an acid and produces a carboxyl group. Such a group is referred to as an acid-dissociable group (I) in the following description.

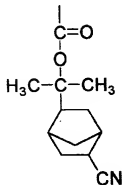
The groups of the following formulas (I-1) to (I-45) can be given as specific examples of preferable acid-dissociable groups (I).



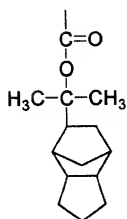
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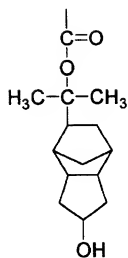
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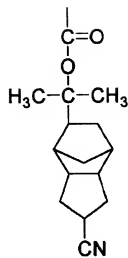
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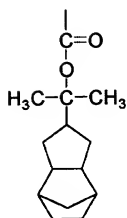
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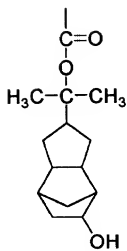
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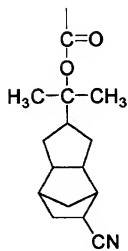
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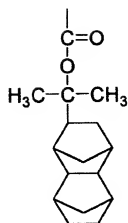
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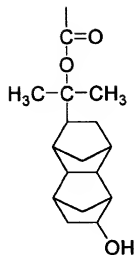
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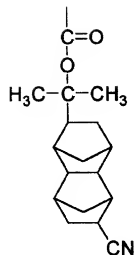
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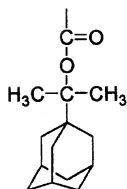
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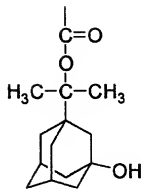
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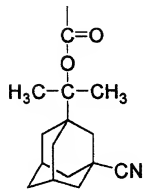
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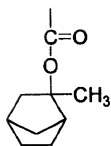
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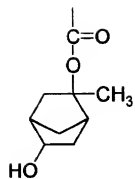
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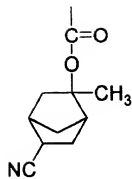
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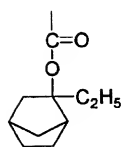
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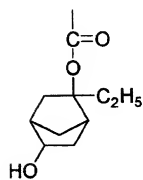
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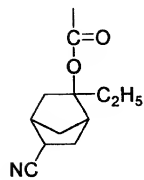
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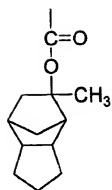
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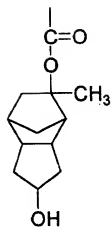
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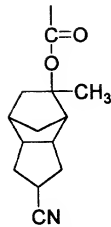
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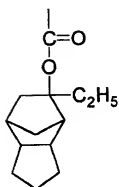
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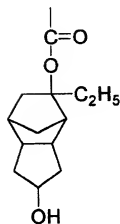
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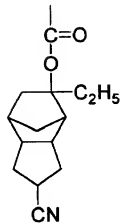
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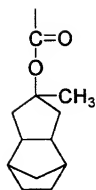


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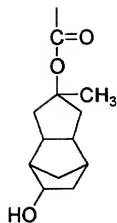


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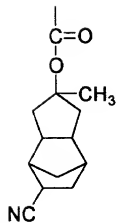




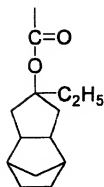
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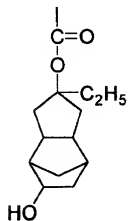
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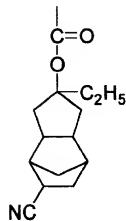
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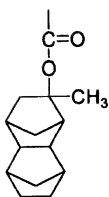
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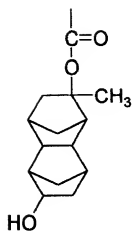
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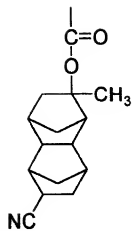
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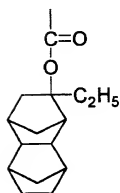
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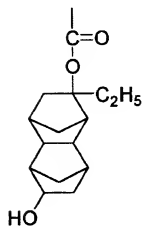
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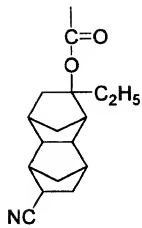
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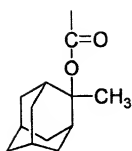
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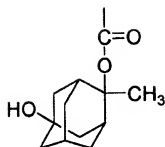
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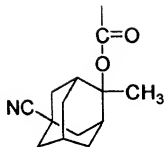
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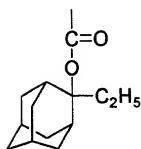
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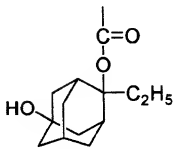
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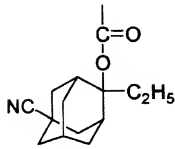
(I-42)



(I-43)



(I-44)



(I-45)

Of these acid-dissociable groups (I), t-butoxycarbonyl group and the groups of the formulas (I-1), (I-2), (I-10), (I-11), (I-13), (I-14), (I-16), (I-17), (I-34), (I-35), (I-40), (I-41), (I-43) or (I-44) are preferable.

The recurring unit (2) is a unit derived from a corresponding (meth)acrylic acid ester.

The resin (A) may comprise one or more recurring units other than the recurring unit (1) and the recurring unit (2) (hereinafter referred to as "other recurring units").

The following compounds can be given as examples of

polymerizable unsaturated monomers which provide other recurring units.

Mono-functional monomers, which include (meth)acrylate having a bridged hydrocarbon skeleton such as norbornyl

(meth)acrylate, isobornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, tetracyclodecanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, adamantly (meth)acrylate, 3-hydroxyadamantyl (meth)acrylate, and adamantylmethyl (meth)acrylate; carboxyl group-containing esters having a

bridged hydrocarbon skeleton of an unsaturated carboxylic acid such as carboxynorbornyl (meth)acrylate, carboxytricyclodecanyl (meth)acrylate, and carboxytetracyclodecanyl (meth)acrylate; other

mono-functional monomers having a bridged hydrocarbon skeleton

such as norbornene (e.g. bicyclo[2.2.1]hept-2-ene),

5-methylbicyclo[2.2.1]hept-2-ene,

5-ethylbicyclo[2.2.1]hept-2-ene,

5-n-propylbicyclo[2.2.1]hept-2-ene,

5-n-butylbicyclo[2.2.1]hept-2-ene,

5-n-pentylbicyclo[2.2.1]hept-2-ene,

5-n-hexylbicyclo[2.2.1]hept-2-ene,

5-hydroxybicyclo[2.2.1]hept-2-ene,

5-hydroxymethylbicyclo[2.2.1]hept-2-ene,

tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-methyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-ethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

8-n-propyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,

- 8-n-butyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-n-pentyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-n-hexyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-hydroxytetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 5 8-hydroxymethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-fluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-fluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-difluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-trifluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 10 8-pentafluoroethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8,8-difluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8,9-difluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8,8-bis(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 15 8,9-bis(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8-methyl-8-trifluoromethyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8,8,9-trifluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 20 8,8,9-tris(trifluoromethyl)tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8,8,9,9-tetrafluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8,8,9,9-tetrakis(trifluoromethyl)tetracyclo-  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 25 8,8-difluoro-9,9-bis(trifluoromethyl)tetracyclo-  
[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,
- 8,9-difluoro-8,9-bis(trifluoromethyl)tetracyclo-

- [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-trifluoro-9-trifluoromethyltetracyclo-  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-trifluoro-9-trifluoromethoxytetracyclo-  
 5 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8,8,9-trifluoro-9-pentafluoropropoxytetracyclo-  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-fluoro-8-pentafluoroethyl-9,9-bis(trifluoromethyl)-  
 tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 10 8,9-difluoro-8-heptafluoroisopropyl-9-trifluoromethyl-  
 tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-chloro-8,9,9-trifluorotetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-  
 ene,  
 8,9-dichloro-8,9-bis(trifluoromethyl)tetracyclo-  
 15 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-(2',2',2'-trifluorocarboethoxytetracyclo-  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 8-methyl-8-(2',2',2'-trifluorocarboethoxy)tetracyclo-  
 [4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodec-3-ene,  
 20 dicyclopentadiene,  
 tricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene,  
 tricyclo[5.2.1.0<sup>2,6</sup>]dec-3-ene,  
 tricyclo[4.4.0.1<sup>2,5</sup>]undec-3-ene,  
 tricyclo[6.2.1.0<sup>1,8</sup>]undec-9-ene,  
 25 tricyclo[6.2.1.0<sup>1,8</sup>]undec-4-ene,  
 tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>.0<sup>1,6</sup>]dodec-3-ene,  
 8-methyltetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>.0<sup>1,6</sup>]dodec-3-ene,

8-ethylidenetetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,12</sup>]dodec-3-ene,  
 8-ethylidenetetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,12</sup>.0<sup>1,6</sup>]dodec-3-ene,  
 pentacyclo[6.5.1.1<sup>3,6</sup>.0<sup>2,7</sup>.0<sup>9,13</sup>]pentadec-4-ene, and  
 pentacyclo[7.4.0.1<sup>2,5</sup>.1<sup>9,12</sup>.0<sup>8,13</sup>]pentadec-3-ene;

- 5 (meth)acrylic acid esters having no hydrocarbon skeleton such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl (meth)acrylate, 2-methylpropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, cyclopropyl (meth)acrylate, cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, 4-methoxycyclohexyl (meth)acrylate, 2-cyclopentylloxycarbonyl ethyl (meth)acrylate, 2-cyclohexylloxycarbonyl ethyl (meth)acrylate, and 2-(4-methoxycyclohexyl)oxycarbonyl ethyl (meth)acrylate;
- 15  $\alpha$ -hydroxymethyl acrylic acid esters such as methyl  $\alpha$ -hydroxymethyl acrylate, ethyl  $\alpha$ -hydroxymethyl acrylate, n-propyl  $\alpha$ -hydroxymethyl acrylate, and n-butyl  $\alpha$ -hydroxymethyl acrylate;
- 20 unsaturated nitril compounds such as (meth)acrylonitrile,  $\alpha$ -chloroacrylonitrile, crotonitrile, maleinitrile, fumaronitrile, mesaconitrile, citraconitrile, and itaconitrile;  
 unsaturated amide compounds such as (meth)acrylamide,
- 25 N,N-dimethyl(meth)acrylamide, crotonamide, maleinamide, fumaramide, mesaconamide, citraconamide, and itaconamide;  
 other nitrogen-containing vinyl compounds such as

N-(meth)acryloylmorpholine, N-vinyl-ε-caprolactam,  
 N-vinylpyrrolidone, vinylpyridine, and vinylimidazole;  
 unsaturated carboxylic acids (anhydrides) such as  
 (meth)acrylic acid, crotonic acid, maleic acid, maleic  
 5 anhydride, fumaric acid, itaconic acid, itaconic anhydride,  
 citraconic acid, citraconic anhydride, and mesaconic acid;  
 carboxyl group-containing esters of unsaturated carboxylic  
 acids having no bridged hydrocarbon skeleton such as  
 2-carboxyethyl (meth)acrylate, 2-carboxypropyl  
 10 (meth)acrylate, 3-carboxypropyl (meth)acrylate,  
 4-carboxybutyl (meth)acrylate, and 4-carboxycyclohexyl  
 (meth)acrylate;  
 α-(meth)acryloyloxy-β-methoxycarbonyl-γ-butyrolactone,  
 α-(meth)acryloyloxy-β-ethoxycarbonyl-γ-butyrolactone,  
 15 α-(meth)acryloyloxy-β-n-propoxycarbonyl-γ-butyrolactone,  
 α-(meth)acryloyloxy-β-i-propoxycarbonyl-γ-butyrolactone,  
 α-(meth)acryloyloxy-β-n-butoxycarbonyl-γ-butyrolactone,  
 α-(meth)acryloyloxy-β-(2-methylpropoxy) carbonyl-γ-  
 butyrolactone,  
 20 α-(meth)acryloyloxy-β-(1-methylpropoxy) carbonyl-γ-  
 butyrolactone,  
 α-(meth)acryloyloxy-β-t-butoxycarbonyl-γ-butyrolactone,  
 α-(meth)acryloyloxy-β-cyclohexyloxy carbonyl-γ-butyrolactone,  
 α-(meth)acryloyloxy-β-(4-t-butylcyclohexyloxy) carbonyl-γ-  
 25 butyrolactone,  
 α-(meth)acryloyloxy-β-phenoxycarbonyl-γ-butyrolactone,  
 α-(meth)acryloyloxy-β-(1-ethoxyethoxy) carbonyl-γ-



butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -(1-cyclohexyloxyethoxy)carbonyl- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -t-butoxycarbonylmethoxycarbonyl- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -tetrahydrofuranyloxycarbonyl- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -tetrahydropyranyloxycarbonyl- $\gamma$ -butyrolactone,

(meth)acryloyloxylactone compounds having an acid-dissociable group such as

$\alpha$ -methoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -ethoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -n-propoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -i-propoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -n-butoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -(2-methylpropoxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  $\alpha$ -(1-methylpropoxy)carbonyl- $\beta$ -(meth)-acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -t-butoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -cyclohexyloxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -(4-t-butylcyclohexyloxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -phoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -(1-ethoxyethoxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  $\alpha$ -(1-cyclohexyloxyethoxy)carbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -t-butoxycarbonylmethoxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,  $\alpha$ -tetrahydrofuranyloxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone, and

$\alpha$ -tetrahydropyranyloxycarbonyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone;

(meth)acryloyloxylactone compound having no acid-dissociable group such as  $\alpha$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -fluoro- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -hydroxy- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -methyl- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -ethyl- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ , $\beta$ -dimethyl- $\gamma$ -butyrolactone,

$\alpha$ -(meth)acryloyloxy- $\beta$ -methoxy- $\gamma$ -butyrolactone,

$\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -fluoro- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -hydroxy- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -methyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -ethyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ , $\alpha$ -dimethyl- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone,

$\alpha$ -methoxy- $\beta$ -(meth)acryloyloxy- $\gamma$ -butyrolactone, and

$\alpha$ -(meth)acryloyloxy- $\delta$ -mevalonolactone; and

compounds in which a carboxyl group in the above unsaturated carboxylic acids or carboxyl group-containing esters having no bridged hydrocarbon skeleton of the above unsaturated

carboxylic acids is converted into the later-described acid-dissociable group (i).

Poly-functional monomers including polyfunctional

monomers having a bridged hydrocarbon skeleton such as 1,2-adamantanediol di(meth)acrylate, 1,3-adamantanediol di(meth)acrylate, 1,4-adamantanediol di(meth)acrylate, and tricyclodecanyldimethylol di(meth)acrylate; and

- 5 polyfunctional monomers having no bridged hydrocarbon skeletons such as methylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 2,5-dimethyl-2,5-hexanediol di(meth)acrylate, 1,8-octanediol di(meth)acrylate, 10 1,9-nonanediol di(meth)acrylate, 1,4-bis(2-hydroxypropyl)benzene di(meth)acrylate, and 1,3-bis(2-hydroxypropyl)benzene di(meth)acrylate.

- The amount of the recurring unit (1) in the resin (A) is usually 10-80 mol%, preferably 20-70 mol%, and still more preferably 30-70 mol% of the total amount of the recurring units. 15 If the amount of the recurring unit (1) is less than 10 mol%, developability and adhesion to substrates of a resist made from the resin tend to decrease. If the amount exceeds 80 mol%, resolution as a resist tends to decrease.

- 20 The amount of the recurring unit (2) is 10-80 mol%, preferably 20-70 mol%, and still more preferably 20-60 mol% of the total amount of the recurring units. If the amount of the recurring unit (2) is less than 10 mol%, resolution as a resist tends to decrease. If the amount exceeds 80 mol%, 25 developability tends to decrease and scum tends to be produced when the resin is used as a resist.

The amount of the other recurring units is usually 50

mol% or less, and preferably 40 mol% or less.

The resin (A) is prepared by polymerizing polymerizable unsaturated monomers corresponding to each of the above recurring units in an appropriate solvent in the presence of a chain transfer agent, as required, using a radical polymerization initiator such as hydroperoxides, dialkyl peroxides, diacyl peroxides, or azo compounds.

As examples of the solvent used for polymerizing the components, alkanes such as n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane; cycloalkanes such as cyclohexane, cycloheptane, cyclooctane, decalin, and norbornane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, and cumene; halogenated hydrocarbons such as chlorobutanes, bromohexanes, dichloroethanes, hexamethylene dibromide, and chlorobenzene; saturated carboxylic acid esters such as ethyl acetate, n-butyl acetate, i-butyl acetate, and methyl propionate; ethers such as tetrahydrofuran, dimethoxyethanes, propyleneglycol monomethylether, and diethoxyethanes; propyleneglycol monomethylether acetate, methylethylketone and the like can be given.

These solvents may be used either individually or in combination of two or more.

The polymerization temperature is usually 40-120°C, and preferably 50-90°C. The reaction time is usually 1-48 hours, and preferably 1-24 hours.

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(hereinafter referred to as "Mw") of the resin (A) determined by gel permeation chromatography (GPC) is usually 3,000-30,000, preferably 5,000-30,000, and still more preferably 5,000-20,000. If Mw of the resin (A) is less than 3,000, heat resistance as a resist tends to decrease. If Mw exceeds 30,000, developability as a resist tends to decrease.

The ratio of Mw to the polystyrene-reduced number average molecular weight (hereinafter referred to as "Mn") determined by gel permeation chromatography (GPC) (Mw/Mn) of the resin (A) is usually 1-5, and preferably 1-3.

It is preferable that the resin (A) contains almost no impurities such as halogens and metals. The smaller the amount of impurities, the better the sensitivity, resolution, process stability, and pattern shape of the resist. The resin (A) may be purified using a chemical purification process such as washing with water or liquid-liquid extraction or a combination of the chemical purification process and a physical purification process such as ultrafiltration or centrifugation, for example.

#### Acid generator (B)

The component (B) of the present invention is a photoacid generator which is a compound of the above-described formula (3) generating an acid upon exposure to light (hereinafter referred to as "acid generator (B)").

The acid generator (B) causes the acid-dissociable group in the resin (A) to dissociate by the action of an acid generated upon exposure. As a result, exposed areas of the resist film

become readily soluble in an alkaline developer, whereby a positive-tone resist pattern is formed.

The following groups are given as examples of the monovalent aromatic hydrocarbon group having 6-20 carbon atoms represented by  $R^5$  in the formula (3): a phenyl group and its derivatives obtained by substituting hydrogen atoms on the ring with a linear or branched alkyl group having 1-6 carbon atoms such as o-tolyl group, m-tolyl group, p-tolyl group,

2,3-dimethylphenyl group, 2,4-dimethylphenyl group,  
2,5-dimethylphenyl group, 2,6-dimethylphenyl group,  
3,4-dimethylphenyl group, 3,5-dimethylphenyl group,  
2,4,6-trimethylphenyl group, and 4-ethylphenyl group; and  
a naphthyl group or a methyl or ethyl-substituted naphthyl group  
such as a 1-naphthyl group, 2-methyl-1-naphthyl group,  
3-methyl-1-naphthyl group, 4-methyl-1-naphthyl group,  
5-methyl-1-naphthyl group, 6-methyl-1-naphthyl group,  
7-methyl-1-naphthyl group, 8-methyl-1-naphthyl group,  
2,3-dimethyl-1-naphthyl group, 2,4-dimethyl-1-naphthyl group,  
2,5-dimethyl-1-naphthyl group, 2,6-dimethyl-1-naphthyl group,  
2,7-dimethyl-1-naphthyl group, 2,8-dimethyl-1-naphthyl group,  
3,4-dimethyl-1-naphthyl group, 3,5-dimethyl-1-naphthyl group,  
3,6-dimethyl-1-naphthyl group, 3,7-dimethyl-1-naphthyl group,  
3,8-dimethyl-1-naphthyl group, 4,5-dimethyl-1-naphthyl group,  
5,8-dimethyl-1-naphthyl group, 4-ethyl-1-naphthyl group,  
1-methyl-2-naphthyl group, 3-methyl-2-naphthyl group, and  
4-methyl-2-naphthyl group.

As substituent in the derivatives of the above-mentioned

aromatic hydrocarbon group, a hydroxyl group; carboxyl group;  
a linear or branched hydroxyalkyl group having 1-4 carbon atoms  
such as a hydroxymethyl group, 1-hydroxyethyl group,  
2-hydroxyethyl group, 3-hydroxypropyl group, and  
5 4-hydroxybutyl group; a linear or branched alkoxyl group having  
1-4 carbon atoms such as a methoxy group, ethoxy group,  
n-propoxy group, i-propoxy group, n-butoxy group,  
2-methylpropoxy group, 1-methylpropoxy group, and t-butoxy  
group; a linear or branched alkoxymethoxy group having 2-5  
10 carbon atoms such as a methoxymethoxy group, ethoxymethoxy  
group, n-propoxymethoxy group, i-propoxymethoxy group,  
n-butoxymethoxy group, and t-butoxymethoxy group; a linear or  
branched 1-alkoxyethoxy group having 3-6 carbon atoms such as  
a 1-methoxyethoxy group, 1-ethoxyethoxy group,  
15 1-n-propoxyethoxy group, 1-i-propoxyethoxy group,  
1-n-butoxyethoxy group, and 1-t-butoxyethoxy group; a linear  
or branched 2-alkoxyethoxy group having 3-6 carbon atoms such  
as a 2-methoxyethoxy group, 2-ethoxyethoxy group,  
2-n-propoxyethoxy group, 2-i-propoxyethoxy group,  
20 2-n-butoxyethoxy group, and 2-t-butoxyethoxy group; a linear  
or branched alkoxycarbonyloxy group having 2-5 carbon atoms  
such as a methoxycarbonyloxy group, ethoxycarbonyl oxy group,  
n-propoxycarbonyloxy group, i-propoxycarbonyloxy group,  
n-butoxycarbonyloxy group, and t-butoxycarbonyloxy group; an  
25 aralkyloxy group having 7-12 carbon atoms such as benzyloxy  
group and phenethyloxy group; an arylacetomethyl group having  
9-15 carbon atoms such phenylacetomethyl group and

1-naphthylacetomethyl group; an oxygen-containing group such as 2-tetrahydrofuran-2-yl group and 2-tetrahydropyran-2-yl group; and a nitrogen-containing group such as cyanomethyl group, 2-cyanoethyl group, 3-cyanopropyl group, and

5 4-cyanobutyl group can be given.

As a monovalent aromatic hydrocarbon group having 6-20 carbon atoms represented by  $R^5$  or the derivatives thereof, 3,5-dimethyl-4-hydroxyphenyl group, 4-methoxyphenyl group, 4-n-butoxyphenyl group, 2,4-dimethoxyphenyl group, 10 3,5-dimethoxyphenyl group, 4-n-butoxy-1-naphthyl group, and the like are preferable.

In the formula (3), 8 or 4 is particularly preferable as the integer  $m$ , and 1 is particularly preferable as the integer  $n$ .

15 The group  $C_mF_{2m+1}$  in the formula (3) is a perfluoroalkyl group having carbon atoms of the number  $m$ . The alkyl group may be either linear or branched.

The following compounds can be given as examples of the acid generator (B) preferably used in the present invention:

20 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium trifluoromethanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium nonafluoro-n-butanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium

25 perfluoro-n-octanesulfonate,

1-(4-n-butoxyphenyl)tetrahydrothiophenium

trifluoromethanesulfonate,



1-(4-n-butoxyphenyl) tetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
1-(4-n-butoxyphenyl) tetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
5 4-hydroxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-hydroxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-hydroxy-1-naphthyltetrahydrothiophenium  
10 perfluoro-n-octanesulfonate,  
4-methoxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-methoxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
15 4-methoxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-ethoxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
4-ethoxy-1-naphthyltetrahydrothiophenium  
20 nonafluoro-n-butanesulfonate,  
4-ethoxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,  
4-n-butoxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,  
25 4-n-butoxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,  
4-n-butoxy-1-naphthyltetrahydrothiophenium

perfluoro-n-octanesulfonate,  
 4-methoxymethoxy-1-naphthyltetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-methoxymethoxy-1-naphthyltetrahydrothiophenium  
 5 nonafluoro-n-butanesulfonate,  
 4-methoxymethoxy-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-ethoxymethoxy-1-naphthyltetrahydrothiophenium  
 trifluoromethanesulfonate,  
 10 4-ethoxymethoxy-1-naphthyltetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-ethoxymethoxy-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 4-(1-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
 15 trifluoromethanesulfonate,  
 4-(1-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-(1-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
 perfluoro-n-octanesulfonate,  
 20 4-(2-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
 trifluoromethanesulfonate,  
 4-(2-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
 nonafluoro-n-butanesulfonate,  
 4-(2-methoxyethoxy)-1-naphthyltetrahydrothiophenium  
 25 perfluoro-n-octanesulfonate,  
 4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
 trifluoromethanesulfonate,

4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

4-methoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

5 4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,

4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

4-ethoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

10 4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,

4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

15 4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,

20 4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

4-i-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
trifluoromethanesulfonate,

25 4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

4-n-butoxycarbonyloxy-1-naphthyltetrahydrothiophenium



4-(2-tetrahydropyranyloxy)-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate, and

4-(2-tetrahydropyranyloxy)-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate.

5 Of these acid generators (B),

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium  
perfluoro-n-octanesulfonate,

10 4-hydroxy-1-naphthyltetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

4-hydroxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

4-n-butoxy-1-naphthyltetrahydrothiophenium  
15 nonafluoro-n-butanesulfonate,

4-n-butoxy-1-naphthyltetrahydrothiophenium  
perfluoro-n-octanesulfonate,

1-(1-naphthylacetomethyl)tetrahydrothiophenium  
nonafluoro-n-butanesulfonate,

20 1-(1-naphthylacetomethyl)tetrahydrothiophenium  
perfluoro-n-octanesulfonate, and the like are particularly  
preferable.

In the present invention, the acid generator (B) may be  
used either individually or in combination of two or more.

25 In the present invention, the following photoacid  
generators (hereinafter referred to as "acid generator (b)")  
can be used in combination with the acid generator (B).

As examples of the acid generator (b), onium salts, halogen-containing compounds, diazoketone compounds, sulfone compounds, sulfonate compounds, and the like can be given.

Examples of the acid generator (b) are given below.

5 Onium salt compounds:

As examples of the onium salt compounds, iodonium salt, sulfonium salt, phosphonium salt, diazonium salt, pyridinium salt, and the like can be given.

Specific examples of onium salt compounds include:

- 10 diphenyliodonium trifluoromethanesulfonate, diphenyliodonium nonafluoro-n-butanesulfonate, diphenyliodonium perfluoro-n-octanesulfonate, bis(4-t-butylphenyl)iodonium trifluoromethanesulfonate, bis(4-t-butylphenyl)iodonium nonafluoro-n-butanesulfonate, 15 bis(4-t-butylphenyl)iodonium perfluoro-n-octanesulfonate, triphenylsulfonium trifluoromethanesulfonate, triphenylsulfonium nonafluoro-n-butanesulfonate, triphenylsulfonium perfluoro-n-octanesulfonate, triphenylsulfonium 10-camphorsulfonate, 20 cyclohexyl·2-oxocyclohexyl·methylsulfonium trifluoromethanesulfonate, dicyclohexyl·2-oxocyclohexylsulfonium trifluoromethanesulfonate, 2-oxocyclohexyldimethylsulfonium trifluoromethanesulfonate, 25 1-naphthyldimethylsulfonium trifluoromethanesulfonate, 1-naphthyldiethylsulfonium trifluoromethanesulfonate, 4-cyano-1-naphthyldimethylsulfonium

trifluoromethanesulfonate,  
4-nitro-1-naphthyldimethylsulfonium  
trifluoromethanesulfonate,  
4-methyl-1-naphthyldimethylsulfonium  
5 trifluoromethanesulfonate,  
4-cyano-1-naphthyldiethylsulfonium  
trifluoromethanesulfonate,  
4-nitro-1-naphthyldiethylsulfonium  
trifluoromethanesulfonate,  
10 4-methyl-1-naphthyldiethylsulfonium  
trifluoromethanesulfonate, and  
4-hydroxy-1-naphthyldimethylsulfonium  
trifluoromethanesulfonate.

Halogen-containing compounds:

15 As examples of halogen-containing compounds, haloalkyl  
group-containing hydrocarbon compounds, haloalkyl  
group-containing heterocyclic compounds, and the like can be  
given.

20 As examples of preferable halogen-containing compounds,  
(trichloromethyl)-s-triazine derivatives such as  
phenylbis(trichloromethyl)-s-triazine,  
4-methoxyphenylbis(trichloromethyl)-s-triazine, and  
1-naphthylbis(trichloromethyl)-s-triazine,  
1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane, and the like  
25 can be given.

Diazoketone compounds:

As examples of diazoketone compounds,

1,3-diketo-2-diazo compounds, diazobenzoquinone compounds, diazonaphthoquinone compounds, and the like can be given.

As examples of preferable diazoketone compounds,

1,2-naphthoquinonediazido-4-sulfonyl chloride,

5 1,2-naphthoquinonediazido-5-sulfonyl chloride,

1,2-naphthoquinonediazido-4-sulfonate or

1,2-naphthoquinonediazido-5-sulfonate of

2,3,4,4'-tetrahydroxybenzophenone,

1,2-naphthoquinonediazido-4-sulfonate or

10 1,2-naphthoquinonediazido-5-sulfonate of

1,1,1-tris(4-hydroxyphenyl)ethane, and the like can be given.

#### Sulfone compounds:

As examples of the sulfone compounds,  $\beta$ -ketosulfone,  $\beta$ -sulfonylsulfone,  $\alpha$ -diazo compounds of these compounds, and

15 the like can be given.

As examples of preferable sulfone compounds,

4-trisphenacylsulfone, mesitylphenacylsulfone,

bis(phenylsulfonyl)methane, and the like can be given.

#### Sulfonate compounds:

20 As examples of the sulfonate compounds, alkyl sulfonate, alkylimide sulfonate, haloalkyl sulfonate, aryl sulfonate, imino sulfonate, and the like can be given.

As examples of preferable sulfone compounds, benzointosylate, tris(trifluoromethanesulfonate) of

25 pyrogallol, nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate, trifluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide,



nonafluoro-n-butanefluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide,

perfluoro-n-octanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarbodiimide,

- 5 N-hydroxysuccinimide trifluoromethanesulfonate,  
N-hydroxysuccinimide nonafluoro-n-butanefluoromethanesulfonate,  
N-hydroxysuccinimide perfluoro-n-octanesulfonate,  
1,8-naphthalenedicarboxylic acid imide  
trifluoromethanesulfonate, 1,8-naphthalenedicarboxylic acid  
10 imide nonafluoro-n-butanefluoromethanesulfonate,  
1,8-naphthalenedicarboxylic acid imide  
perfluoro-n-octanesulfonate, and the like can be given.

Of these acid generators (b), the following compounds are preferable: diphenyliodonium trifluoromethanesulfonate,

- 15 diphenyliodonium nonafluoro-n-butanefluoromethanesulfonate,  
diphenyliodonium perfluoro-n-octanesulfonate,  
bis(4-t-butylphenyl)iodonium trifluoromethanesulfonate,  
bis(4-t-butylphenyl)iodonium nonafluoro-n-butanefluoromethanesulfonate,  
bis(4-t-butylphenyl)iodonium perfluoro-n-octanesulfonate,  
20 triphenylsulfonium trifluoromethanesulfonate,  
triphenylsulfonium nonafluoro-n-butanefluoromethanesulfonate,  
triphenylsulfonium perfluoro-n-octanesulfonate,  
cyclohexyl-2-oxocyclohexylmethylsulfonium  
trifluoromethanesulfonate, dicyclohexyl-2-oxo  
25 cyclohexylsulfonium trifluoromethanesulfonate,  
2-oxocyclohexyldimethylsulfonium trifluoromethanesulfonate,  
4-hydroxy-1-naphthyl dimethylsulfonium trifluoromethane

5 sulfonate,  
trifluoromethanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
dicarbodiimide,  
nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
10 dicarbodiimide,  
perfluoro-n-octanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-  
dicarbodiimide, N-hydroxysuccinimido  
trifluoromethanesulfonate, N-hydroxysuccinimido  
nonafluoro-n-butanesulfonate, N-hydroxysuccinimido  
15 perfluoro-n-octanesulfonate, and 1,8-naphthalenedicarboxylic  
acid imide trifluoromethanesulfonate.

The acid generators (b) may be used either individually or in combination of two or more.

20 The total amount of the acid generator (B) and the acid generator (b) used in the radiation-sensitive resin composition of the present invention is usually 0.1-20 parts by weight, and preferably 0.5-10 parts by weight for 100 parts by weight of the resin (A) from the viewpoint of ensuring sensitivity and developability as a resist. If this total amount is less than  
25 0.1 part by weight, sensitivity and developability tend to decrease. If the amount exceeds 20 parts by weight, a rectangular resist pattern may not be obtained due to decreased radiation transmittance.

The proportion of the acid generator (b) to be added is  
30 80 wt% or less, and preferably 60 wt% or less of the total amount of the acid generator (B) and the acid generator (b). If the proportion of the acid generator (b) exceeds 80 wt%, the desired

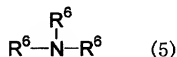
effects of the present invention may be impaired.

It is preferable to add an acid diffusion controller to the radiation-sensitive resin composition of the present invention. The acid diffusion controller controls diffusion of an acid generated from the acid generator (B) or acid generator (b) upon exposure in the resist film to hinder unfavorable chemical reactions in the unexposed area.

The addition of such an acid diffusion controller improves storage stability of the resulting radiation-sensitive resin composition and resolution as a resist. Moreover, the addition of the acid diffusion controller prevents the line width of the resist pattern from changing due to changes in the post-exposure delay (PED) between exposure and development, whereby a composition with remarkably superior process stability can be obtained.

As the acid diffusion controller, organic compounds containing nitrogen of which the basicity does not change during exposure or heating for forming a resist pattern are preferable.

As examples of such nitrogen-containing organic compounds, a compound shown by the following formula (5) (hereinafter called "nitrogen-containing compound (a)"),



wherein R<sup>6</sup> individually represents a hydrogen atom, a

substituted or unsubstituted, linear, branched, or cyclic alkyl group, substituted or unsubstituted aryl group, or substituted or unsubstituted aralkyl group, a compound having two nitrogen atoms in the molecule (hereinafter referred to as

- 5 "nitrogen-containing compound (b)"), a polyamino compound having three or more nitrogen atoms in the molecule (hereinafter referred to as "nitrogen-containing compound (c)"), amide group-containing compound, urea compound, nitrogen-containing heterocyclic compound, and the like can be given.

- 10 As examples of the nitrogen-containing compounds (a), mono(cyclo)alkylamines such as n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, and cyclohexylamine; di(cyclo)alkylamines such as di-n-butylamine, di-n-pentylamine, di-n-hexylamine, di-n-heptylamine,  
15 di-n-octylamine, di-n-nonylamine, di-n-decylamine, cyclohexylmethylamine, and dicyclohexylamine; tri(cyclo)alkylamines such as triethylamine, tri-n-propylamine, tri-n-butylamine, tri-n-pentylamine, tri-n-hexylamine, tri-n-heptylamine, tri-n-octylamine,  
20 tri-n-nonylamine, tri-n-decylamine, cyclohexyldimethylamine, methyldicyclohexylamine, and tricyclohexylamine; aromatic amines such as aniline, N-methylaniline, N,N-dimethylaniline, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-nitroaniline, diphenylamine, triphenylamine, and  
25 naphthylamine; and the like can be given.

Examples of the nitrogen-containing compound (b) include ethylenediamine, N,N,N',N'-tetramethylethylenediamine,

tetramethylenediamine, hexamethylenediamine,  
 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether,  
 4,4'-diaminobenzophenone, 4,4'-diaminodiphenylamine,  
 2,2-bis(4-aminophenyl)propane,  
 5 2-(3-aminophenyl)-2-(4-aminophenyl)propane,  
 2-(4-aminophenyl)-2-(3-hydroxyphenyl)propane,  
 2-(4-aminophenyl)-2-(4-hydroxyphenyl)propane,  
 1,4-bis[1-(4-aminophenyl)-1-methylethyl]benzene,  
 1,3-bis[1-(4-aminophenyl)-1-methylethyl]benzene,  
 10 bis(2-dimethylaminoethyl)ether,  
 bis(2-diethylaminoethyl)ether, and the like.

As examples of the nitrogen-containing compounds (c),  
 polyethyleneimine, polyallylamine, a polymer of  
 2-dimethylaminoethylacrylamide, and the like can be given.

15 As examples of the amide group-containing compounds,  
 N-t-butoxycarbonyl di-n-octylamine, N-t-butoxycarbonyl  
 di-n-nonylamine, N-t-butoxycarbonyl di-n-decylamine,  
 N-t-butoxycarbonyl dicyclohexylamine,  
 N-t-butoxycarbonyl-1-adamantylamine, N-t-butoxycarbonyl-N-  
 20 methyl-1-adamantylamine,  
 N,N-di-t-butoxycarbonyl-1-adamantylamine,  
 N,N-di-t-butoxycarbonyl-N-methyl-1-adamantylamine,  
 N-t-butoxycarbonyl-4,4'-diaminodiphenylmethane,  
 N,N'-di-t-butoxycarbonylhexamethylenediamine,  
 25 N,N,N'N'-tetra-t-butoxycarbonylhexamethylenediamine,  
 N,N'-di-t-butoxycarbonyl-1,7-diaminoheptane,  
 N,N'-di-t-butoxycarbonyl-1,8-diaminooctane,

N,N'-di-t-butoxycarbonyl-1,9-diaminononane,  
N,N'-di-t-butoxycarbonyl-1,10-diaminodecane,  
N,N'-di-t-butoxycarbonyl-1,12-diaminododecane,  
N,N'-di-t-butoxycarbonyl-4,4'-diaminodiphenylmethane,

- 5 N-t-butoxycarbonylbenzimidazole,  
N-t-butoxycarbonyl-2-methylbenzimidazole, and  
N-t-butoxycarbonyl-2-phenylbenzimidazole;  
formamide, N-methylformamide, N,N-dimethylformamide,  
acetamide, N-methylacetamide, N,N-dimethylacetamide,  
10 propionamide, benzamide, pyrrolidone, N-methylpyrrolidone;  
and the like can be given.

- As examples of the urea compounds, urea, methylurea,  
1,1-dimethylurea, 1,3-dimethylurea, 1,1,3,3-tetramethylurea,  
1,3-diphenylurea, tri-n-butylthiourea, and the like can be  
15 given. Examples of the nitrogen-containing heterocyclic  
compounds include: imidazoles such as imidazole, benzimidazole,  
4-methylimidazole, 4-methyl-2-phenylimidazole, and  
N-t-butoxycarbonyl-2-phenylbenzimidazole; pyridines such as  
pyridine, 2-methylpyridine, 4-methylpyridine,  
20 2-ethylpyridine, 4-ethylpyridine, 2-phenylpyridine,  
4-phenylpyridine, 2-methyl-4-phenylpyridine, nicotine,  
nicotinic acid, nicotinamide, quinoline, 4-hydroxyquinoline,  
8-oxyquinoline, and acridine; piperazines such as piperazine,  
1-(2-hydroxyethyl)piperazine; pyrazine, pyrazole, pyridazine,  
25 quinoxaline, purine, pyrrolidine, piperidine,  
3-piperidino-1,2-propanediol, morpholine, 4-methylmorpholine,  
1,4-dimethylpiperazine, and 1,4-diazabicyclo[2.2.2]octane;

and the like.

Of these nitrogen-containing organic compounds, the nitrogen-containing compounds (a), nitrogen-containing compounds (b), and nitrogen-containing heterocyclic compounds are preferable.

The acid diffusion controller may be used either individually or in combination of two or more.

The amount of the acid diffusion controller to be added is usually 15 parts by weight or less, preferably 10 parts by weight or less, and still more preferably 5 parts by weight or less for 100 parts by weight of the resin (A). If the proportion of the acid diffusion controller exceeds 15 parts by weight, sensitivity as a resist and developability of the exposed area tend to decrease. If the amount is less than 0.001 part by weight, the pattern shape or dimensional accuracy as a resist may decrease depending on the processing conditions.

An alicyclic additive having an acid-dissociable group may be added to the radiation-sensitive resin composition of the present invention to further improve dry etching resistance, pattern shape, adhesion to substrate, and the like.

The following compounds can be given as examples of the alicyclic additives: adamantane derivatives such as t-butyl 1-adamantanecarboxylate, t-butoxycarbonylmethyl 1-adamantanecarboxylate, di-t-butyl 1,3-adamantanedicarboxylate, t-butyl 1-adamantaneacetate, t-butoxycarbonylmethyl 1-adamantaneacetate, di-t-butyl

1,3-adamantanediacetate, and  
2,5-dimethyl-2,5-di(adamantylcarbonyloxy)-n-hexane;  
deoxycholates such as t-butyl deoxycholate,  
t-butoxycarbonylmethyl deoxycholate, 2-ethoxyethyl  
5 deoxycholate, 2-cyclohexyloxyethyl deoxycholate,  
3-oxocyclohexyl deoxycholate, tetrahydropyranyl deoxycholate,  
and mevalonolactone deoxycholate;  
lithocholates such as t-butyl lithocholate,  
t-butoxycarbonylmethyl lithocholate, 2-ethoxyethyl  
10 lithocholate, 2-cyclohexyloxyethyl lithocholate,  
3-oxocyclohexyl lithocholate, tetrahydropyranyl lithocholate,  
and mevalonolactone lithocholate; and the like.

These alicyclic additives may be used either  
individually or in combination of two or more.

15 The amount of the alicyclic additives to be added is  
usually 50 parts by weight or less, and preferably 30 parts by  
weight or less for 100 parts by weight of the resin (A). If  
the amount of alicyclic additives exceeds 50 parts by weight,  
heat resistance as a resist tends to decrease.

20 Surfactants which improve applicability, developability,  
or the like may be added to the radiation-sensitive resin  
composition of the present invention.

As examples of surfactants, nonionic surfactants such  
as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether,  
25 polyoxyethylene oleyl ether, polyoxyethylene n-octyl phenyl  
ether, polyoxyethylene n-nonyl phenyl ether, polyethylene  
glycol dilaurate, polyethylene glycol distearate;



commercially available products such as KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.), Polyflow No. 75, No. 95 (manufactured by Kyo-eisha Chemical Co., Ltd.), FTOP EF301, EF303, EF352 (manufactured by TOHKEM PRODUCTS CORPORATION), MEGAFAF F171, F173 (manufactured by Dainippon Ink and Chemicals, Inc.), Florard FC430, FC431 (manufactured by Sumitomo 3M Ltd.), Asahi Guard AG710, Surflon S-382, SC-101, SC-102, SC-103, SC-104, SC-105, SC-106 (manufactured by Asahi Glass Co., Ltd.); and the like can be given.

These surfactants may be used either individually or in combination of two or more.

The amount of surfactants to be added is usually 2 parts by weight or less for 100 parts by weight of the total of the resin (A), acid generator (B), and acid generator (b).

As other additives, halation inhibitors, adhesion promoters, storage stabilizers, anti-foaming agents, and the like can be given.

#### Preparation of composition solution

The radiation-sensitive resin composition of the present invention is prepared as a composition solution by dissolving the composition in a solvent so that the total solid content is 5-50 wt%, and preferably 10-25 wt%, and filtering the composition using a filter with a pore diameter of about 0.2  $\mu\text{m}$ , for example.

Examples of solvents used for the preparation of the composition solution include: linear or branched ketones such as 2-butanone, 2-pentanone, 3-methyl-2-butanone, 2-hexanone,

4-methyl-2-pentanone, 3-methyl-2-pentanone,  
3,3-dimethyl-2-butanone, 2-heptanone, and 2-octanone;  
cyclic ketones such as cyclopentanone, 3-methylcyclopentanone,  
cyclohexanone, 2-methylcyclohexanone,

5 2,6-dimethylcyclohexanone, and isophorone;  
propylene glycol monoalkyl ether acetates such as propylene  
glycol monomethyl ether acetate, propylene glycol monoethyl  
ether acetate, propylene glycol mono-n-propyl ether acetate,  
propylene glycol mono-i-propyl ether acetate, propylene glycol  
10 mono-n-butyl ether acetate, propylene glycol mono-i-butyl  
ether acetate, propylene glycol mono-sec-butyl ether acetate,  
and propylene glycol mono-t-butyl ether acetate;

alkyl 2-hydroxypropionates such as methyl 2-hydroxypropionate,  
ethyl 2-hydroxypropionate, n-propyl 2-hydroxypropionate,  
15 i-propyl 2-hydroxypropionate, n-butyl 2-hydroxypropionate,  
i-butyl 2-hydroxypropionate, sec-butyl 2-hydroxypropionate,  
and t-butyl 2-hydroxypropionate;

alkyl 3-alkoxypropionates such as methyl 3-methoxypropionate,  
ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, and  
20 ethyl 3-ethoxypropionate;

n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, t-butyl  
alcohol, cyclohexanol, ethylene glycol monomethyl ether,  
ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl  
ether, ethylene glycol mono-n-butyl ether, diethylene glycol  
25 dimethyl ether, diethylene glycol diethyl ether, diethylene  
glycol di-n-propyl ether, diethylene glycol di-n-butyl ether,  
ethylene glycol monomethyl ether acetate, ethylene glycol

monoethyl ether acetate, ethylene glycol mono-n-propyl ether acetate, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, toluene, xylene, 2-hydroxy-2-methylethyl propionate, ethoxyethyl acetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutyrate, 3-methoxybutylacetate, 3-methyl-3-methoxybutylacetate, 3-methyl-3-methoxybutylpropionate, 3-methyl-3-methoxybutylbutyrate, ethyl acetate, n-propyl acetate, n-butylacetate, methyl acetoacetate, ethyl acetoacetate, methyl pyruvate, ethyl pyruvate, N-methyl pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, benzyl ethyl ether, di-n-hexyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, caproic acid, caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate,  $\gamma$ -butyrolactone, ethylene carbonate, propylene carbonate; and the like.

These solvents may be used either individually or in combination of two or more. Among these solvents, linear or branched ketones, cyclic ketones, propylene glycol monoalkyl ether acetates, alkyl 2-hydroxypropionates, and alkyl 3-alkoxypropionates are preferable.

#### Formation of resist pattern

The radiation-sensitive resin composition of the present invention is particularly useful as a chemically-amplified resist.

In the chemically-amplified resist, an acid-dissociable group in the resin (A) dissociates by the action of an acid generated from the acid generator (B) or a mixture of the acid generator (B) and acid generator (b) upon exposure, thereby producing a carboxyl group. As a result, solubility of the exposed part of the resist in an alkaline developer increases, whereby the exposed part is dissolved in an alkaline developer and removed to obtain a positive-tone resist pattern.

A resist pattern is formed from the radiation-sensitive resin composition of the present invention by applying the composition solution to, for example, substrates such as a silicon wafer or a wafer coated with aluminum using an appropriate application method such as rotational coating, cast coating, and roll coating to form a resist film. The resist film is then optionally pre-baked (hereinafter called "PB") and exposed to form a predetermined resist pattern. As radiation used for exposure, visible rays, ultraviolet rays, deep ultraviolet rays, X-rays, electron beams, or the like are appropriately selected depending on types of the acid generator. It is particularly preferable to use an ArF excimer laser (wavelength: 193 nm) or KrF excimer laser (wavelength: 248 nm). An ArF excimer laser (wavelength: 193 nm) is particularly preferable.

In the present invention, it is preferable to perform post-exposure bake (hereinafter called "PEB"). PEB ensures smooth dissociation of the acid-dissociable group in the resin (A). The heating temperature for PEB is usually 30-200°C, and

preferably 50-170°C, although the heating conditions vary depending on the composition of the radiation-sensitive resin composition.

In order to bring out latent capability of the radiation-sensitive resin composition of the present invention, an organic or inorganic anti-reflection film may be formed on a substrate as disclosed in Japanese Patent Publication No. 12452/1994, for example. Moreover, a protection film may be formed on the resist film as disclosed in Japanese Patent Publication No. 188598/1993, for example, in order to prevent the effects of basic impurities or the like in an environmental atmosphere. These techniques may be employed in combination.

The exposed resist film is then developed to form a predetermined resist pattern.

As examples of a developer used for development, it is preferable to use an alkaline aqueous solution prepared by dissolving at least one of alkaline compounds such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia, ethylamine, n-propylamine, diethylamine, di-n-propylamine, triethylamine, methyldiethylamine, ethyldimethylamine, triethanolamine, tetramethylammonium hydroxide, pyrrole, piperidine, choline, 1,8-diazabicyclo-[5.4.0]-7-undecene, and 1,5-diazabicyclo-[4.3.0]-5-nonene.

The concentration of the alkaline aqueous solution is usually 10 wt% or less. If the concentration of the alkaline aqueous solution exceeds 10 wt%, an unexposed area may be

dissolved in the developer.

Organic solvents or the like may be added to the developer containing an alkaline aqueous solution.

As examples of organic solvents, ketones such as acetone, methyl ethyl ketone, methyl i-butyl ketone, cyclopentanone, cyclohexanone, 3-methylcyclopentanone, and 2,6-dimethylcyclohexanone; alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, t-butyl alcohol, cyclopentanol, cyclohexanol, 1,4-hexanediol, and 1,4-hexanedimethylol; ethers such as tetrahydrofuran and dioxane; esters such as ethyl acetate, n-butyl acetate, and i-amyl acetate; aromatic hydrocarbons such as toluene and xylene; phenol, acetylacetone, dimethylformamide; and the like can be given.

These organic solvents may be used either individually or in combination of two or more.

The amount of the organic solvents is preferably 100 vol% or less of the alkaline aqueous solution. If the amount of the organic solvents exceeds 100 vol%, an exposed area may remain undeveloped due to decreased developability.

In addition, surfactants or the like may be added to the developer containing the alkaline aqueous solution in an appropriate amount.

The resist film is generally washed with water after development using a developer containing an alkaline aqueous solution.

### EXAMPLES

The embodiments of the present invention will be described in more detail by examples. However, these examples should not be construed as limiting the present invention.

In the examples, part(s) refers to part(s) by weight unless otherwise indicated. Measurement and evaluation of each composition in the examples and comparative examples were carried out as follows.

#### Mw:

Mw was measured by gel permeation chromatography (GPC) using GPC columns (manufactured by Tosoh Corp., G2000HXL x 2, G3000HXL x 1, G4000HXL x 1) under the following conditions. Flow rate: 1.0 ml/minute, eluate: tetrahydrofuran, column temperature: 40°C, standard reference material: monodispersed polystyrene

#### Radiation transmittance:

A solution composition was applied to a quartz plate and the coating was post-baked on a hot plate at 90°C for 60 seconds to obtain a resist film with a thickness of 0.4 µm. Radiation transmittance of the resist film was calculated from absorbance at a wavelength of 193 nm and was adopted as a standard for transparency in the deep UV ray region.

#### Sensitivity:

A solution composition was applied to a silicon wafer (ARC) with a 520Å thick Deep UV30J film (manufactured by Brewer Science Corp.) coated on the surface by spin coating and post-baked on a hot plate under the conditions shown in Table

2 to obtain a resist coating with a thickness of 0.4  $\mu\text{m}$ . The coating was exposed to radiation through a mask pattern using an ArF excimer laser exposure apparatus (manufactured by Nikon Corp., lens numerical aperture: 0.55, wavelength: 193 nm).

5 After PEB under the conditions shown in Table 2, the resist coatings were developed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution (Examples 1-7) or 2.38 x 1/50 wt% tetramethylammonium hydroxide aqueous solution (Comparative Example 1) at 25°C for 1 minute, washed with water, and dried  
10 to form a positive-tone resist pattern. An optimum dose capable of forming a 0.16  $\mu\text{m}$  line-and-space pattern (1L1S) with a 1:1 line width was taken as sensitivity.

#### Resolution:

15 Minimum dimensions of the resist pattern resolved at the optimum dose were taken as the resolution.

#### Dry-etching resistance:

A composition solution was applied to a silicon wafer by spin coating and dried to form a resist film with a thickness of 0.5  $\mu\text{m}$ . Then, the resist film was dry-etched using a Pinnacle  
20 8000 (manufactured by PMT Co.) and with  $\text{CF}_4$  as an etching gas at a flow rate of 75 sccm and an output of 2,500 W under a gas pressure of 2.5 mTorr to measure the etching rate. The relative etching rate was evaluated assuming that the etching rate of the resist film formed from the resin composition solution of  
25 Comparative Example 1 is 1.0. The smaller the etching rate, the better the dry-etching resistance.

#### Pattern configuration:



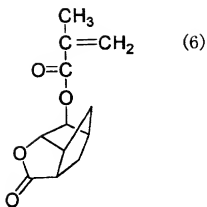
The dimensions of the lower side  $L_1$  and the upper side  $L_2$  of the rectangular cross-section of a line and space pattern (1L1S) with a line width of  $0.16\mu\text{m}$  were measured using a scanning electron microscope. A pattern shape which satisfied a formula

5 " $0.85 \leq L_2/L_1 \leq 1$ " and was straight with no extended skirt was evaluated as "Good", and otherwise evaluated as "Bad".

#### Synthesis Example 1

30 g of a compound of the following formula (6) and 20 g of 2-methyl-2-adamantyl methacrylate were dissolved in 50 g of tetrahydrofuran to obtain a homogeneous solution. After bubbling nitrogen for 30 minutes through the solution, 3 g of azobisisobutyronitrile was added as an initiator. The mixture was heated to  $65^\circ\text{C}$ . The mixture was stirred for 6 hours at this

15 temperature. After the reaction, the reaction solution was cooled to room temperature and diluted with 50 g of tetrahydrofuran. The diluted solution was poured into 1,000 ml of n-hexane. The precipitated white powder was collected by filtration and dried to obtain a resin.



This resin was a copolymer with an Mw of 12,000,  
 containing recurring units derived from the compound of the  
 formula (6) and 2-methyl-2-adamantyl methacrylate in the amount  
 of 60 mol% and 40 mol%, respectively. This resin is referred  
 to as a "resin (A-1)".

#### Synthesis Example 2

28 g of the compound of the above formula (6), 21 g of  
 2-methyl-2-adamantyl methacrylate, and 1 g of  
 N,N-dimethylacrylamide were dissolved in 50 g of  
 tetrahydrofuran to obtain a homogeneous solution. After  
 bubbling nitrogen for 30 minutes through the solution, 3 g of  
 azobisisobutyronitrile was added as an initiator. The mixture  
 was heated to 65°C. The mixture was stirred for 6 hours at this  
 temperature. After the reaction, the reaction solution was  
 cooled to room temperature and diluted with 50 g of  
 tetrahydrofuran. The diluted solution was poured into 1,000  
 ml of n-hexane. The precipitated white powder was collected  
 by filtration and dried to obtain a resin.

This resin was a copolymer with an Mw of 13,000, containing recurring units derived from the compound of the formula (6), 2-methyl-2-adamantyl methacrylate, and N,N-dimethylacrylamide in the amount of 55 mol%, 40 mol%, and 5 mol%, respectively. This resin is referred to as a "resin (A-2)".

### Synthesis Example 3

15 g of the compound of the above formula (6), 20 g of 2-methyl-2-adamantyl methacrylate, and 15 g of 3-hydroxyadamantly acrylate were dissolved in 50 g of tetrahydrofuran to obtain a homogeneous solution. After bubbling nitrogen for 30 minutes through the solution, 3 g of azobisisobutyronitrile was added as an initiator. The mixture was heated to 65°C. The mixture was stirred for 6 hours at this temperature. After the reaction, the reaction solution was cooled to room temperature and diluted with 50 g of tetrahydrofuran. The diluted solution was poured into 1,000 ml of n-hexane. The precipitated white powder was collected by filtration and dried to obtain a resin. This resin was a copolymer with an Mw of 11,000, containing recurring units derived from the compound of the formula (6), 2-methyl-2-adamantyl methacrylate, and 3-hydroxyadamantly acrylate in the amount of 30 mol%, 40 mol%, and 30 mol%, respectively. This resin is referred to as a "resin (A-3)".

### Synthesis Example 4

30 g of a compound of the above formula (6) and 20 g of 2-norbornyl-2-n-propyl acrylate were dissolved in 50 g of

5 tetrahydrofuran to obtain a homogeneous solution. After  
bubbling nitrogen for 30 minutes through the solution, 3 g of  
azobisisobutyronitrile was added as an initiator. The mixture  
was heated to 65°C. The mixture was stirred for 6 hours at this  
10 temperature. After the reaction, the reaction solution was  
cooled to room temperature and diluted with 50 g of  
tetrahydrofuran. The diluted solution was poured into 1,000  
ml of n-hexane. The precipitated white powder was collected  
by filtration and dried to obtain a resin.

10 This resin was a copolymer with an Mw of 12,600,  
containing recurring units derived from the compound of the  
formula (6) and 2-norbornyl-2-n-propyl acrylate in the amount  
of 60 mol% and 40 mol%, respectively. This resin is referred  
to as a "resin (A-4)".

#### 15 Synthesis Example 5

20 22 g of the compound of the above formula (6), 18 g of  
2-methyl-2-adamantyl methacrylate, 4 g of maleic anhydride, and  
6 g of norbornene were dissolved in 50 g of tetrahydrofuran to  
obtain a homogeneous solution. After bubbling nitrogen for 30  
25 minutes through the solution, 3 g of azobisisobutyronitrile was  
added as an initiator. The mixture was heated to 65°C. The  
mixture was stirred for 6 hours at this temperature. After the  
reaction, the reaction solution was cooled to room temperature  
and diluted with 50 g of tetrahydrofuran. The diluted solution  
30 was poured into 1,000 ml of n-hexane. The precipitated white  
powder was collected by filtration and dried to obtain a resin.

This resin was a copolymer with an Mw of 6,300, containing

recurring units derived from the compound of the formula (6),  
2-methyl-2-adamantyl methacrylate, maleic anhydride, and  
norbornene in the amount of 40 mol%, 30 mol%, 15 mol%, and 15  
mol%, respectively. This resin is referred to as a "resin  
5 (A-5)".

#### Synthesis Example 6

25 g of a compound of the above formula (6) and 25 g of  
2-methyl-2-adamantyl methacrylate were dissolved in 50 g of  
tetrahydrofuran to obtain a homogeneous solution. After  
10 bubbling nitrogen for 30 minutes through the solution, 3 g of  
azobisisobutyronitrile was added as an initiator. The mixture  
was heated to 65 °C. The mixture was stirred for 6 hours at  
this temperature. After the reaction, the reaction solution  
was cooled to room temperature and diluted with 50 g of  
15 tetrahydrofuran. The diluted solution was poured into 1,000  
ml of n-hexane. The precipitated white powder was collected  
by filtration and dried to obtain a resin.

This resin was a copolymer with an Mw of 11,000,  
containing recurring units derived from the compound of the  
20 formula (6) and 2-methyl-2-adamantyl methacrylate in the amount  
of 50 mol% and 50 mol% respectively. This resin is referred  
to as a resin (A-6).

#### Synthesis Example 7

15 g of the compound of the above formula (6), 22.5 g  
25 of 2-methyl-2-adamantyl methacrylate, and 12.5 g of  
3-hydroxyadamantyl acrylate were dissolved in 50 g of  
tetrahydrofuran to obtain a homogeneous solution. After

1064000.011602  
bubbling nitrogen for 30 minutes through the solution, 3 g of azobisisobutyronitrile was added as an initiator. The mixture was heated to 65 °C. The mixture was stirred for 6 hours at this temperature. After the reaction, the reaction solution  
5 was cooled to room temperature and diluted with 50 g of tetrahydrofuran. The diluted solution was poured into 1,000 ml of n-hexane. The precipitated white powder was collected by filtration and dried to obtain a resin. This resin was a copolymer with an Mw of 11,000, containing recurring units  
10 derived from the compound of the formula (6), 2-methyl-2-adamantyl methacrylate, and 3-hydroxyadamantyl acrylate in the amount of 30 mol%, 45 mol% and 25 mol%, respectively. This resin is referred to as a resin (A-7).

#### Synthesis Example 8

15 28.75 g of the compound of the above formula (6), 28.75 g of 2-methyl-2-adamantyl methacrylate, and 2.5 g of methacrylic acid were dissolved in 50 g of tetrahydrofuran to obtain a homogeneous solution. After bubbling nitrogen for 30 minutes through the solution, 3 g of azobisisobutyronitrile was  
20 added as an initiator. The mixture was heated to 65 °C. The mixture was stirred for 6 hours at this temperature. After the reaction, the reaction solution was cooled to room temperature and diluted with 50 g of tetrahydrofuran. The diluted solution was poured into 1,000 ml of n-hexane. The precipitated white  
25 powder was collected by filtration and dried to obtain a resin. This resin was a copolymer with an Mw of 13,000, containing recurring units derived from the compound of the formula (6),

2-methyl-2-adamantyl methacrylate, and methacrylic acid in the amount of 47.5 mol%, 47.5 mol%, and 5 mol% respectively. This resin is referred to as a resin (A-8).

Examples 1-12 and Comparative Example 1

- 5           Composition solutions including components shown in Table 1 were evaluated. The evaluation results are shown in Table 3.

Components other than the polymers (A-1) to (A-5) shown in Table 1 are as follows.

10   Other resins

a-1: t-Butyl methacrylate/methyl methacrylate/methacrylic acid copolymer (copolymerization molar ratio = 40/40/20, Mw = 20,000)

Acid generator (B)

- 15    B-1: 4-n-butoxy-1-naphthyltetrahydrothiophenium nonafluoro-n-butanesulfonate
- B-2: 1-(3,5-dimethyl-4-hydroxyphenyl)tetrahydrothiophenium nonafluoro-n-butanesulfonate
- B-3: 4-n-butoxy-1-naphthyltetrahydrothiophenium
- 20    perfluoro-n-octanesulfonate

Acid generator (b)

- b-1: triphenylsulfonium trifluoromethanesulfonate
- b-2: triphenylsulfonium nonafluoro-n-butanesulfonate
- b-3: bis(4-t-butylphenyl)iodonium
- 25    nonafluoro-n-butanesulfonate
- b-4: nonafluoro-n-butanesulfonylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide

Acid diffusion controller

C-1: tri-n-octylamine

C-2: methyldicyclohexylamine

C-3: 3-piperidino-1,2-propanediol

5 C-4: N-t-butoxycarbonyldicyclohexylamine

C-5: N-t-butoxycarbonyl-2-phenylbenzimidazole

Other additives

D-1: t-butyl deoxycholate

D-2: di-t-butyl 1,3-adamantanedicarboxylate

10 D-3: t-butoxycarbonylmethyl deoxycholate

Solvent

E-1: 2-heptanone

E-2: cyclohexanone

E-3: propylene glycol monomethyl ether acetate

15 E-4: ethyl 3-ethoxypropionate



Table 1

Unit in parenthesis: part by weight

	Resin	Acid generator	Acid diffusion controller	Other additives	Solvent
Example 1	A-1 (100)	B-1 (2.0) b-1 (1.0)	C-1 (0.10)		E-1 (530)
Example 2	A-1 (80) A-2 (10)	B-1 (3.0)	C-4 (0.05)	D-1 (10)	E-1 (430) E-2 (100)
Example 3	A-3 (95)	B-2 (2.0) b-2 (20)	C-2 (0.10)	D-2 (5)	E-1 (430) E-4 (100)
Example 4	A-2 (10) A-3 (80)	B-3 (3.0) B-3 (2.0)	C-3 (0.10)	D-3 (10)	E-3 (530)
Example 5	A-4 (100)	B-1 (2.0) b-4 (3.0)	C-5 (0.05)		E-1 (530)
Example 6	A-5 (90)	B-3 (2.0) b-4 (2.0)	C-5 (0.05)	D-3 (10)	E-1 (430) E-2 (100)
Example 7	A-2 (10) A-5 (80)	B-2 (3.0) b-4 (2.0)	C-3 (0.05) C-5 (0.03)	D-2 (10)	E-3 (430) E-4 (100)
Example 8	A-6 (90)	B-3 (51.1)	C-5 (0.10)	D-3 (10)	E-3 (530)
Example 9	A-7 (100)	B-2 (5.0)	C-5 (0.10)		E-1 (530)
Example 10	A-B (90)	B-3 (5.0)	C-5 (0.10)	D-3 (10)	E-3 (530)
Example 11	A-7 (100)	B-2 (4.0) b-2 (1.0)	C-5 (0.10)		E-1 (430) E-2 (100)
Example 12	A-1 (90)	B-3 (5.0)	C-5 (0.10)	D-3 (10)	E-3 (530)
Comparative Example 1	a-1 (90)	b-1 (2.0)	C-1 (0.05)	D-1 (10)	E-1 (530)

Table 2

	Resist film thickness ( $\mu\text{m}$ )	Substrate	PB		PEB	
			Temp ( $^{\circ}\text{C}$ )	Time (sec)	Temp ( $^{\circ}\text{C}$ )	Time (sec)
Example 1	0.4	ARC	130	90	140	90
Example 2	0.4	ARC	130	90	140	90
Example 3	0.4	ARC	130	90	140	90
Example 4	0.4	ARC	130	90	140	90
Example 5	0.4	ARC	130	90	140	90
Example 6	0.4	ARC	130	90	140	90
Example 7	0.4	ARC	130	90	140	90
Example 8	0.4	ARC	130	90	140	90
Example 9	0.4	ARC	130	90	140	90
Example 10	0.4	ARC	130	90	140	90
Example 11	0.4	ARC	130	90	140	90
Example 12	0.4	ARC	130	90	140	90
Comparative Example I	0.4	ARC	130	90	140	90

Table 3

	Radiation transmittance (193 nm, %)	Sensitivity (J/m <sup>2</sup> )	Resolution (μm)	Dry-etching resistance	Pattern configuration
Example 1	72	89	0.15	0.8	Good
Example 2	74	95	0.15	0.6	Good
Example 3	69	79	0.15	0.7	Good
Example 4	70	85	0.15	0.8	Good
Example 5	69	81	0.15	0.5	Good
Example 6	73	86	0.15	0.7	Good
Example 7	72	92	0.15	0.6	Good
Example 8	71	90	0.15	0.8	Good
Example 9	68	79	0.15	0.7	Good
Example 10	71	90	0.15	0.8	Good
Example 11	67	81	0.15	0.7	Good
Example 12	70	95	0.14	0.8	Good
Comparative Example 1	61	150	0.18	1.0	Good

The radiation-sensitive resin composition of the present invention exhibits high transparency and excellent resolution when used as a chemically-amplified resist responsive to active radiation such as deep ultraviolet rays represented by a KrF excimer laser (wavelength: 248 nm) and an ArF excimer laser (wavelength: 193 nm). The resist exhibits high resolution, excellent dry etching resistance, superior sensitivity, pattern shape, and adhesion to the substrate. The resin composition is suitably used for fabrication of integrated circuit devices which are expected to be more and more miniaturized.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings.

It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than

5 as specifically described herein.